DEVELOPMENT AND APPLICATIONS OF FLOW INJECTION METHODS BASED ON IODOMETRIC REACTIONS

by

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LIST OF ABBREVIATION

2-NPOE	2-nitrophenyl octyl ether
4-NPH	4-nitrophenylhydrazine
ABTS	2,2-azino-bis-3-ethylbenzothialine-6-sulfonate
AV	Anisidine Value
CAC	Combined available chlorine
CE	Capillary electrophoresis
DPD	Diethyl-p-phenylenediamine
DSC	Differential scanning calorimetry
FAC	Free available chlorine
FI	Flow injection
FIA	Flow injection analysis
FTIR	Fourier transformed infrared
HPLC	High performance liquid chromatography
IC	Indigo carmine
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ISE	Ion selective electrode
IV	Iodine Value
LOV	Lab on valve
MCFIA	Multi-commutated flow injection analysis

MSFIA	Multi-syringe flow injection analysis
MPFS	Multiple pump flow system
MO	Methyl orange
NIR	Near infrared
ODS	*o*-dianisidne
OT	*o*-toluidine
PTFE	Poly(tetrafluoroethylene)
PV	Peroxide Value
PVC	Polyvinyl chloride
R.S.D	Relative standard deviation
S/N	Signal to noise ratio
SIA	Sequential injection analysis
SIC	Sequential injection chromatography
SPE	Solid phase extraction
SYR	Syringaldazine
TAC	Total available chlorine
TCPO	bis(2,4,6-(trichlorophenyl)oxalate)
TGA	Thermogravimetric analysis

PEMBANGUNAN DAN APLIKASI KAEDAH SUNTIKAN ALIRAN BERDASARKAN TINDAK BALAS IODOMETRI

ABSTRAK

Tesis ini fokus kepada pembangunan kaedah analisis suntikan aliran (FIA) berdasarkan tindak balas iodometri klasik. Kaedah serba boleh ini yang merangkumi penggunaan pengesan aliran potensiometri I_3^- dan pengukuran I_2 secara spektrofotometri telah ditunjukkan dalam analisis pantas sampel farmaseutikal (benzilpenisilin), alam sekitar (spesies klorin) dan minyak sayuran (nilai iodin – (IV), nilai peroksida – (PV) dan nilai anisidina – (AV)). Dalam bab 2, satu reaktor enzim penisilas telah dimasukkan ke dalam sistem FIA untuk memangkinkan hidrolisis benzilpenisilin untuk menghasilkan asid penisiloik yang seterusnya akan menggunakan I_3^-. Asid penisiloik dicampurkan dengan aliran I_3^- di mana I_3^- yang berlebihan akan dikesan oleh pengesan I_3^-. Di bawah keadaan sistem yang diadaptasikan, kekerapan pensampelan sebanyak 75 sampel per jam diperolehi. Gerak balasnya adalah linear dari 0.05 ke 1.0 mM (n = 4) dan had pengesananya ialah 0.0025 mM. Keboleh ulangan semula yang baik (R.S.D 3.80 % (n = 4)) diperolehi bagi penentuan 0.5 mM benzilpenisilin.

Sistem FIA dibangunkan untuk membolehkan penspesiasan klorin bebas (FAC), klorin bergabung (CAC), klorin total (TAC) dan klorit dengan menggunakan pengesan yang sama. Penspesiasan dilakukan melalui diskriminasi kinetik antara FAC dan CAC dengan menggunakan Fe^{2+}. Penspesiasan klorin dengan klorit boleh dicapai dengan menggunakan

sistem yang sama tetapi dengan menggunakan aliran yang berbeza pH. Kaedah ini adalah linear dari 2.8 x 10^{-6} ke 2.8 x 10^{-4} M klorin aktif (ditunjukkan sebagai OCl^-) dengan had pengesanan 1.4 x 10^{-4} M. Kepilihan kaedah ini dikaji dengan menyiasat pH minimum bagi pengoksidaan iodida oleh pengoksida, dan juga dengan mengkaji pekali kepilihan potensiometri.

Pembangunan kaedah FIA untuk penentuan IV, PV and AV dalam minyak sayuran juga dilaksanakan. Kaedah FIA-spektrofotometri yang pantas bagi penentuan IV juga dibentangkan. Apabila beroperasi dalam keadaan yang terubahsuai, graf penentukuran adalah linear dari 17 ke 100 IV. Kekerapan pensampelan adalah 15 sampel per jam dan puncak ulangan semula ditunjukkan oleh R.S.D ialah 4.50 % (n = 4). Untuk penentuan PV, kalium iodida (KI) dicampurkan dan dioksidakan oleh hidroperoksida dalam minyak dengan menggunakan vorteks di mana I_3^- yang dihasilkan diaspirasikan ke dalam lintasan aliran larutan tampan asetat dan dikesani oleh pengesan I_3^-. Tatacara FIA yang optimum adalah linear dari 0.35 – 28.0 PV (meq O_2/kg) dengan had pengesanan 0.32 PV. Keboleh ulangan semula yang baik (R.S.D 2.70 % (n = 8) untuk penentuan 1.1 PV) dan kadar persampelan 80 sampel per jam diperolehi. Untuk penentuan AV, kloramina-T diperkenalkan dan digunakan oleh komponen 2-alkenal dalam minyak, dan campuran dicampur dengan menggunakan pencampuren vorteks. Kloramina-T yang berlebihan diaspirasikan ke dalam lintasan aliran larutan tampan asetat. Kloramina-T akan mengoksidakan ion iodida dalam sistem tampan untuk menghasilkan I_3^- yang boleh dikesan pengesan I_3^- yang sama. Tatacara yang optimum ini adalah linear dari 1.0 – 23.0 AV (had pengesanan ialah 0.9 AV) dan ia menunjukkan keboleh ulangan yang baik (R.S.D 3.16 %

(n = 4) untuk penentuan 5.0 AV) dengan kadar persampelan 40 sampel per jam. Kesan saiz reaktor tindak balas, pH dan kepekatan reagen, masa vorteks, masa pemisahan fasa, kadar aliran sampel dan pH aliran pembawa untuk sistem PV dan AV telah dikaji. Penentuan turutan kedua-dua PV dan AV dengan menggunakan pengesan I_3^- yang sama juga dibentangkan bagi penentuan nilai TOTOX (TOTOX = 2PV + AV). Kedua-dua sistem telah digabungkan dalam satu konfigurasi FIA di mana kedua-dua parameter (PV dan AV) ditentukan secara turutan menggunakan injap penukaran yang mengarahkan aliran reagen yang diperlukan.

DEVELOPMENT AND APPLICATIONS OF FLOW INJECTION METHODS BASED ON IODOMETRIC REACTIONS

ABSTRACT

This thesis is focused on the development of flow injection analysis (FIA) methologies based on the classical iodometric reactions. The versatility of the approaches involving the use of a flow through I_3^- potentiometric detector and the measurement of I_2 spectrophotometrically is demonstrated for the rapid analysis of pharmaceutical (benzylpenicillin), environmental (chlorine species) and vegetable oil (Iodine Value – (IV), Peroxide Value – (PV) and Anisidine Value - (AV)) samples. In chapter 2, a penicillase enzyme reactor was incorporated into the FIA system to catalyse the hydrolysis of benzylpenicillin to produce penicilloic acid that subsequently consumes I_3^-. The penicilloic acid was merged with the I_3^- solution and the excess I_3^- was detected by the I_3^- sensor. Under the adopted conditions, a sampling frequency of 75 samples h^{-1} was obtained. The response was linear from 0.05 to 1.0 mM (n = 4) benzylpenicillin and the limit of detection was 0.0025 mM. Good reproducibility (R.S.D 3.80 % (n = 4)) was obtained for the determination of 0.5 mM benzylpenicillin.

A FIA system was developed that allowed the speciation of free available chlorine (FAC), combined available chlorine (CAC), total available chlorine (TAC) and chlorite using the same detector. The speciation was effected by the kinetic discrimination of FAC and CAC using Fe^{2+}. The speciation of available chlorine species and chlorite can be achieved by

using the same set up but employing a flow stream of different pH. The method exhibited linearity from 2.8 x 10^{-6} to 2.8 x 10^{-4} M active chlorine (expressed as OCl^-) with detection limit of 1.4 x 10^{-4} M. The selectivity of the method was studied by examining the minimum pH for the oxidation of iodide by different oxidants, and also by assessing the potentiometric selectivity coefficients.

The developments of FIA methods for the determination of IV, PV and AV in vegetable oils were also carried out. A FIA-spectrophotometric method for the rapid determination of IV is also described. When operated under the adopted conditions calibration graph was linear from 17 to 100 IV. The sampling frequency was 15 samples h^{-1} and the reproducibility of peak height obtained as expressed by the R.S.D was 4.50 % (n = 4). For the determination of PV, potassium iodide (KI) was mixed and was oxidized by hydroperoxide in oils through vortex action. The I_3^- produced was aspirated into an acetate buffer flow system and was detected by I_3^- detector. The optimized FIA procedure was linear over 0.35 – 28.0 PV (meq O_2/kg) with a detection limit of 0.32 PV. Good reproducibility (R.S.D. of 2.70% (n = 8) for the determination of 1.1 PV) and sampling rate of 80 samples h^{-1} was obtained. For the determination of AV, chloramine-T was introduced and was consumed by 2-alkenals component in the oils; the mixtures were thoroughly mixed by vortex action. The excessive chloramine-T was aspirated into an acetate buffer in the flow system. Chloramine-T oxidized the iodide ions in the buffer system to produce I_3^- that was sensed by the I_3^- detector. The optimized procedure is linear over 1.0 – 23.0 AV (detection limit 0.9 AV) and it exhibit good reproducibility (R.S.D. of 3.16 % (n = 4) for the determination of 5.0 AV) with a sampling rate of 40 samples h^{-1}.